

3. Organic polymers are modeled as flexible chains whose links are rigid segments of length b that can pivot freely relative to each other. In the random walk approximation, the effects of overlaps between the links are ignored and the polymer configurations are taken to resemble random paths of N steps.

Take it as given that, for a simple random walk:

- i) the end to end distance $R(N)$ scales as $R(N) \approx b\sqrt{N}$.
ii) the probability of landing at \vec{R} after N steps (starting at the origin) is $\approx e^{-R^2/(2Nb^2)}$ (up to irrelevant pre-factors).

- (a) At the level of the random walk approximation, what is the *entropy* of the idealized polymer of N units with total length R ?
- (b) The polymer's self energy is modeled by a (repulsive) energy $\lambda > 0$ for any two units that come within a fixed distance from each other (and zero contribution otherwise). Assuming that the polymer's units are spread relatively uniformly over a volume of diameter R , obtain an approximate expression for the polymer's *free energy* showing the dependence on λ , b , N , R and T (powers or simple functions). (You do not need to specify the constant coefficients.)
- (c) Minimizing the free energy, derive a relation of the form: $\langle R \rangle \approx N^\nu$ for the order of magnitude estimate of the equilibrium end-to-end distance of the self-repelling polymer (at fixed b and $\lambda > 0$), in d dimensions. What value does the approximate expression for the free energy yield for the *exponent* ν ?

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$$a) P \sim e^{-R^2/2Nb^2} = P_0 e^{-R^2/2Nb^2} = \frac{\Omega(R)}{\Omega_0}, \Omega(R) = \Omega_0 P_0 e^{-R^2/2Nb^2}$$

$$S(R) = k_B \ln[\Omega_0 P_0 e^{-R^2/2Nb^2}] = k_B \ln(\Omega_0 P_0) - \frac{k_B R^2}{2Nb^2} \leftarrow k_B \ln(\Omega_0 P_0) \equiv S_0 \\ = -\frac{k_B R^2}{2Nb^2} + S_0$$

$$S(R) = -\frac{k_B R^2}{2Nb^2} + S_0$$

$$b) F = U_{\text{scat}} - S T$$

$$\downarrow U_{\text{scat}} = \lambda \frac{\frac{4}{3}\pi N b^3}{\frac{4}{3}\pi R^3} = \lambda N \frac{b^3}{R^3} \\ = \lambda N \frac{b^3}{R^3} + \frac{k_B T R^2}{2Nb^2} - S_0 T$$

$$F = \lambda N \frac{b^3}{R^3} + \frac{k_B T R^2}{2Nb^2} - S_0 T$$

$$c) F = \lambda N \frac{b^d}{R^{d+2}} + \frac{k_B T R^2}{2Nb^2} - S_0 T$$

$$\frac{\partial F}{\partial R} = -d \lambda N \frac{b^d}{R^{d+2}} + \frac{k_B T}{Nb^2} R = 0$$

$$\frac{k_B T}{Nb^2} R^{d+2} = d \lambda N b^d \leftarrow \frac{1}{k_B T} \equiv \beta$$

$$R^{d+2} = \beta d \lambda b^{d+2} N^2$$

$$R = (\beta d \lambda)^{\frac{2}{d+2}} b N^{\frac{2}{d+2}} \propto N^{\frac{2}{d+2}} = N^{\nu}$$

$$\nu = \frac{2}{d+2}$$